Biogeosciences Discuss., 12, 9369–9391, 2015 www.biogeosciences-discuss.net/12/9369/2015/ doi:10.5194/bgd-12-9369-2015 © Author(s) 2015. CC Attribution 3.0 License.



This discussion paper is/has been under review for the journal Biogeosciences (BG). Please refer to the corresponding final paper in BG if available.

# Insights into the transfer of silicon isotopes into the sediment record

V. N. Panizzo<sup>1,2</sup>, G. E. A. Swann<sup>1,2</sup>, A. W. Mackay<sup>3</sup>, E. Vologina<sup>4</sup>, M. Sturm<sup>5</sup>, V. Pashley<sup>6</sup>, and M. S. A. Horstwood<sup>6</sup>

<sup>1</sup>School of Geography, Centre for Environmental Geochemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, UK

<sup>2</sup>Centre for Environmental Geochemistry, British Geological Survey, Nottingham, NG12 5GG, UK

<sup>3</sup>Environmental Change Research Centre, Department of Geography, University College London, Gower Street, London, WC1E 6BT, UK

<sup>4</sup>Institute of Earth's Crust, Siberian Branch of the Russian Academy of Sciences, 128 ul. Lermontov, Irkutsk, 664033, Russia

<sup>5</sup>Eawag-ETH, Swiss Federal Institue of Aquatic Science and Technology, 8600, Dübendorf, Switzerland

<sup>6</sup>NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK



Received: 22 May 2015 – Accepted: 02 June 2015 – Published: 23 June 2015 Correspondence to: V. N. Panizzo (virginia.panizzo@nottingham.ac.uk) Published by Copernicus Publications on behalf of the European Geosciences Union.



### Abstract

The first  $\delta^{30}$ Si<sub>diatom</sub> data from lacustrine sediment traps are presented from Lake Baikal, Siberia. Data are compared with March surface water (upper 180 m)  $\delta^{30}$ Si<sub>DSi</sub> compositions for which a mean value of  $+2.28\% \pm 0.09$  (95% confidence) is de-5 rived. This value acts as the pre-diatom bloom baseline isotopic composition of waters  $(\delta^{30}Si_{DSi initial})$ . Open traps were deployed along the depth of the Lake Baikal south basin water column between 2012–2013. Diatom assemblages display a dominance (> 85 %) of the spring bloom species Synedra acus var radians, so that  $\delta^{30}$ Si<sub>diatom</sub> compositions reflect spring bloom utilisation. Diatoms were isolated from open traps and in addition, from 3 monthly (sequencing) traps (May, June and July 2012) for  $\delta^{30}$ Si<sub>diatom</sub> 10 analyses. Mean  $\delta^{30}$ Si<sub>diatom</sub> values for open traps are +1.23‰ ± 0.06 (at 95% confidence and MSWD of 2.9, n = 10) and, when compared with mean upper water  $\delta^{30}$ Si<sub>DSi</sub> signatures, suggest a diatom fractionation factor ( $\epsilon_{uptake}$ ) of -1.05 %, which is in good agreement with published values from oceanic and other freshwater systems. The near constant  $\delta^{30}$ Si<sub>diatom</sub> compositions in open traps demonstrates the full preservation of 15 the signal through the water column and thereby justifies the use and application of the technique in biogeochemical and palaeoenvironmental research. Data are finally compared with lake sediment core samples, collected from the south basin. Values of  $\pm 1.30\% \pm 0.08$  (2 $\sigma$ ) and  $\pm 1.43\% \pm 0.13$  (2 $\sigma$ ) were derived for cores BAIK13-1C (0.6–0.8 cm core depth) and at BAIK13-4F (0.2–0.4 cm core depth), respectively. Trap 20 data highlight the absence of a fractionation factor associated with diatom dissolution  $(e_{dissolution})$  down the water column and in the lake surface sediments, thus validating the application of  $\delta^{30}$ Si<sub>diatom</sub> analyses in Lake Baikal and other freshwater systems, in palaeoreconstructions.



#### 1 Introduction

Records of diatom silicon isotopes (δ<sup>30</sup>Si<sub>diatom</sub>) provide a key means to investigate changes in the global silicon cycle (De La Rocha, 2006; Hendry and Brzezinski, 2014; Leng et al., 2009; Tréguer and De La Rocha, 2013). Through measurements of δ<sup>30</sup>Si (including diatoms; δ<sup>30</sup>Si<sub>diatom</sub> and the dissolved silicon (DSi) phase; δ<sup>30</sup>Si<sub>DSi</sub>) it has been possible to elucidate a more comprehensive understanding of biogeochemical cycling both on continents (e.g., Cockerton et al., 2013; Opfergelt et al., 2011) and in the ocean (Fripiat et al., 2012) allowing, for example, an assessment of the role of the marine biological pump in regulating past changes in atmospheric *p*CO<sub>2(aq)</sub>
(e.g., Pichevin et al., 2009). These studies and their interpretations rely on work that has examined the mechanics of diatom silicon isotope fractionation, demonstrating a fractionation factor (ε<sub>uptake</sub>) of -1.1‰ ± 0.4 to -1.2‰ ± 0.2 that is independent of temperature, *p*CO<sub>2(aq)</sub> and other vital effects (De La Rocha et al., 1997; Fripiat et al., 2011; Milligan et al., 2004; Varela et al., 2004)

<sup>15</sup> A further assumption is that the isotopic signatures captured by diatoms in the photic zone are faithfully transported through the water column and into the sediment record, without alteration from dissolution or other processes. This has been questioned by evidence from diatom cultures which have revealed a diatom dissolution induced fractionation ( $\epsilon_{dissolution}$ ) of  $-0.55 \pm 0.05$ % that is independent of inter-species variations or temperature (Demarest et al., 2009), although the importance and indeed existence of an  $\epsilon_{dissolution}$  has been questioned by studies in the natural environment (Egan et al., 2010 Whited et al., 2014). While the processes of  $s^{30}$  Dimensional distribution of the statement of the st

2012; Wetzel et al., 2014). Whilst measurements of  $\delta^{30}$ Si<sub>diatom</sub> from sediment traps (Varela et al., 2004; Fripiat et al., 2011, 2012) and core-tops (Egan et al., 2012) in marine systems have been used in isolation, an integrated record is needed to document the fate of  $\delta^{30}$ Si<sub>diatom</sub> as diatoms sink through the water and become incorporated into the sediment record, particularly in a lacustrine system where hitherto no such work has taken place. Here, we present pre-diatom bloom  $\delta^{30}$ Si<sub>DSi initial</sub> and  $\delta^{30}$ Si<sub>diatom</sub> data from Lake Baikal, Siberia (Fig. 1). By analysing samples from sediment traps through



the > 1600 m water column and a sediment core from the same site (Fig. 1), we document the perfect transfer of the photic zone  $\delta^{30}$ Si<sub>DSi</sub> signature into diatoms and into the sediment record.

#### 2 Lake Baikal

- Lake Baikal (103°43′-109°58′ E and 51°28′-55°47′ N) is the world's deepest and most voluminous lake (23615 km<sup>3</sup>) containing one fifth of global freshwater not stored in glaciers and ice caps (Gronskaya and Litova, 1991; Sherstyankin et al., 2006). Divided into three basins (south, central and north) the Academician Ridge separates the central (max depth 1642 m) and north (max depth 904 m) basins while the Buguldeika ridge
- <sup>10</sup> running north-easterly from the shallow waters of the Selenga delta, divides the south (max depth 1460 m) and central basins (Sherstyankin et al., 2006) (Fig. 1). This study will focus on the southern basin (where sediment traps were deployed; Fig. 1), which has an estimated average depth of 853 m (Sherstyankin et al., 2006) and a long water residency time of 377–400 years (Gronskaya and Litova, 1991), although the residency
- time of silicon in the lake is estimated to be shorter at 170 years (Falkner et al., 1997). Diatom dissolution in Lake Baikal occurs mainly at the bottom sediment-water interface as opposed to during down-column settling of diatoms (Ryves et al., 2003) with Müller et al. (2005) showing that remineralisation processes are an important constituent of surface water nutrient renewal. Lake Baikal may be thought of as having
- two differing water masses with the mesothermal maximum (MTM) separating them at a depth of c. 200–300 m (Kipfer and Peeters, 2000; Ravens et al., 2000). In the upper waters (above c. 200–300 m) both convective and wind forced mixing occurs twice a year (Shimaraev et al., 1994; Troitskaya et al., 2014) during spring and autumn overturn periods. These overturn periods proceed (precede) ice off (on) respectively and and autumn over-two periods proceed (precede) ice off (on) respectively and (precede) ice off (precede) ice off
- <sup>25</sup> are separated by a period of summer surface water stratification (e.g. above the MTM). Diatom productivity in the lake is most notable during these overturn periods although spring diatom blooms tend to dominate annual productivity. Below c. 300 m (e.g. be-



low the MTM) waters are permanently stratified (Ravens et al., 2000; Shimaraev et al., 1994; Shimaraev and Granin, 1991) although despite this the water column of Lake Baikal is oxygenated throughout and it is estimated that c. 10 % of its deeper water is renewed each year through downwelling episodes (Hohmann et al., 1997; Kipfer et al., 1996; Shimaraev et al., 1993; Weiss et al., 1991).

#### 3 Methods

## 3.1 Sample locations

Upper water column (top 180 m) samples for DSi concentrations and  $\delta^{30}$ Si<sub>DSi</sub> analyses were collected on two occasions, when the lake was ice-covered, less than two weeks apart, in March 2013 at site BAIK13-1 (sampling a and b; Table 1) in the south basin of Lake Baikal (Fig. 1; 51.76778° N and 104.41611° E) using a 2 litre Van Dorn sampler. This sampling coincided with the period when: (1) riverine and precipitation inflows to the lake are minimal; and (2) photosynthetic activity in the lake was low (as demonstrated by negligible in-situ chlorophyll *a* measurements). We argue that the average of these captured, pre-bloom, DSi and  $\delta^{30}$ Si<sub>DSi</sub> values represent the baseline nutrient conditions of the upper waters of the South Basin. Samples were filtered on collection through 0.4 µm polycarbonate filters (Whatman) before storage in 125 mL acidwashed LDPE bottles and acidified with Superpure HCl to a pH above 2.

At the same site, samples were collected from open sediment traps (n = 10) de-<sup>20</sup> ployed by EAWAG and the Institute of Earth's Crust/SB-RAS between March 2012 and March 2013 (from 100 to 1350 m water depth; Table 2) and from monthly sequencing traps (n = 3) on the same array at a water depth of 100 m. For all open traps and for three of the monthly traps (A4: 17 May 2012 to 07 June 2012, A6: 04 July 2012 to 31 July 2012 and A7: 31 July 2012 to 21 August 2012) it was possible to extract <sup>25</sup> sufficient diatoms for isotope analysis (see below).



Sediment cores were collected from site BAIK13-1 (51.76778° E and 104.41611° N; Fig. 1) and from the nearby BAIK13-4 (51.69272° N and 104.30003° E; Fig. 1) using a UWITEC corer through c. 78–90 cm of ice with on site sub-sampling at 0.25 cm intervals. Both sediment cores were dated using <sup>210</sup>Pb dating (at University College London) using the CRS (constant rate of supply) model (Appleby and Oldfield, 1978), which is in agreement with the individual <sup>137</sup>Cs record for the two cores. Sub-samples corresponding to 0.6–0.8 cm at BAIK13-1 (core BAIK13-1C; age = 2007 AD ± 2 years) and 0.2–0.4 cm at BAIK13-4 (core BAIK13-4F; age = 2012 AD ± 7 years: the sampling period covered by the sediment traps) were processed to obtain diatoms for  $\delta^{30}$ Si<sub>diatom</sub> analysis.

# 3.2 Analytical methods

# 3.2.1 Diatom counting

25

To assess the taxonomic composition of diatoms in the sediment trap samples, diatom slides were prepared using a protocol that omits any chemical treatments or centrifu-<sup>15</sup> gation in order to minimise further diatom dissolution and valve breakage (see Mackay et al., 1998 for full details). Slides were counted using a Zeiss light microscope with oil immersion and phase contrast at ×1000 magnification. Microspheres at a known concentration of  $8.2 \times 10^6$ , were added to all samples in order to calculate diatom concentrations.

# 20 3.2.2 Silicon isotope sample preparation

Prior to isotope analysis 0.7–1.0 g of sediment core and trap material was digested of organic matter with analytical grade  $H_2O_2$  (30%) at 75°C for c. 12h. This was followed by heavy density separation using sodium polytungstate (Sometu Europa) at 2500 rpm for fifteen minutes, with centrifuge break off, at a specific gravity between 2.10–2.25 g mL<sup>-1</sup> (adjusted to suit sample contamination) to remove lithogenic



particles and clays. Samples were washed (up to 10 times) with deionised water at 2500 rpm for five minutes before visual inspection for contaminants at  $\times -400$  magnification on a Zeiss inverted light microscope. All samples showed no evidence of external contaminants that would impact the isotopic measurements.

- Silicon concentrations on all 25 samples (10 March lake water and 13 diatom opal trap samples (Z and A traps) and 2 lake surface sediment samples) were measured on an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Agilent Technologies 7500) at the British Geological Survey. Diatom samples were digested using the NaOH fusion method (Georg et al., 2006) with 1–3 mg of powdered material fused with
- <sup>10</sup> a 200 mg NaOH (Quartz Merk) pellet in a silver crucible, covered within a Ni crucible with lid, for 10 min in a muffle furnace at 730 °C. Following fusion, silver crucibles were placed in a 30 mL Teflon Savillex beaker and rinsed with Milli Q water before adding Ultra Purity Acid (UPA) HCI (Romil) to reach a pH above 2. Samples were sonicated to ensure they were fully dissolved and mixed before leaving overnight in the dark.
- <sup>15</sup> Water samples with DSi concentrations < 1.5 ppm were pre-concentrated prior to column chemistry by evaporating 30 mL of sample to 5 mL at 70 °C on a hotplate in a Teflon Savillex beaker in a laminar flow hood. This follows Hughes et al. (2011), who showed no evaporative alteration of silicon in samples and reference materials, provided samples are not evaporated to dryness. This was not conducted for sample BAIK1a-100 m
- as there was insufficient sample to do so (Table 1). Following pre-concentration, samples (and reference and validation materials) were purified by passing a known volume (between 1 and 2.5 mL depending on Si concentration) through a 1.8 mL cationic resin bed (BioRad AG50W-X12) (Georg et al., 2006) and eluted with 3 mL of Milli Q water in order to obtain an optimal Si concentration of between 3–10 ppm.

#### 25 3.2.3 Silicon isotope analysis

All isotope analyses were carried out on a ThermoScientific Neptune Plus MC-ICP-MS (multi collector inductively coupled plasma mass spectrometer), operated in wetplasma mode using the method/settings outlined in Cockerton et al. (2013). To over-



come any analytical bias due to differing matrices, samples and reference materials were acidified using HCI (to a concentration of 0.05 M, using Romil UPA) and sulphuric acid (to a concentration of 0.003 M, using Romil UPA) following the recommendations of Hughes et al. (2011) the principle being that doping samples and standards alike, above and beyond the natural abundance of  $CI^-$  and  $SO_4^{2-}$ , will evoke a similar mass bias response in each. All samples and reference materials were doped with ~ 300 ppb magnesium (Mg, Alfa Aesar SpectraPure) to allow the data to be corrected for the ef-

- fects of instrument induced mass bias (Cardinal et al., 2003; Hughes et al., 2011). In order to do this Mg concentrations were the same in both standard and samples.
- Background signal contributions on <sup>28</sup>Si were typically between 50 and 100 mV. Total procedural blanks for water samples were variable but up to 50 ng compared to typical sample amounts of 1750–4000 ng. Typical <sup>28</sup>Si signals were up to 100 mV, (c. 3 mV <sup>30</sup>Si). Blank compositions were typically within 1–2‰ of sample compositions, measured to a precision of ca. 1‰. Taking a worse-case scenario of a 0.5% composi-
- tional variation between sample and blank, procedural blanks may have contributed a c. 0.06–0.15‰ shift in typical sediment or water sample composition respectively. This increases to a c. 0.60‰ compositional shift in exceptional cases i.e. for one sample replicate (BAIK13-1, 100 m) which has a silicon concentration much less than 1 ppm. Fusion procedural blanks were up to 70 ng compared to typical fusion sample amounts
- of 3500–5500 ng. Using the same procedural blank compositional estimation, shifts of less than 0.1 ‰ are expected in the sample compositions. The potential impact of the total procedural blank is therefore well within the uncertainty limits of the data.

Following Mg mass bias correction, NBS-28 was used to correct the data using sample-standard bracketing. A reference material (Diatomite) was analysed repeat-

<sup>25</sup> edly for validation during each analytical session and a previously determind material matrix-matched to the samples (an in-house river water sample, RMR4) was also periodically analysed to ensure long-term consistency of data sets. Data were corrected on-line for mass bias using an exponential function, assuming <sup>24</sup>Mg/<sup>25</sup>Mg = 0.126633. All uncertainties are reported at  $2\sigma$  absolute, and incorporate an excess variance de-



rived from the Diatomite validation material, which was quadratically added to the analytical uncertainty of each measurement.  $\delta^{30}\text{Si}:\delta^{29}\text{Si}$  ratios of all data were compared with the mass dependent fractionation line (1.93), with which all data comply (Johnson et al., 2004). Long term (~ 2 years) reproducibility for the method is: Diatomite = +1.23‰ ± 0.18 (2 SD, *n* = 220) (consensus value of +1.26‰ ± 0.2, 2 $\sigma$ ; Reynolds et al., 2007) and RMR4 = +0.88‰ ± 0.20 (2 SD, *n* = 42).

#### 4 Results

Below ice  $\delta^{30}$ Si<sub>DSi</sub> and DSi values in March 2013 from the top 1 m of the water column, collected within 2 weeks of each other, are +2.34‰ ±0.15 (2 $\sigma$ ), 1.22 ppm and +2.16‰ ±0.09 (2 $\sigma$ ), 0.74 ppm for BAIK13-1a and BAIK13-1b respectively (Fig. 2; Table 1). DSi compositions show some variability with depth at both sites, with overall trends showing decreasing concentrations with depth (Fig. 2), with the exception of the surface sample at BAIK13-1b (0.74 ppm). As will be discussed in Sect. 5.1, the weighted mean surface water (e.g. above the MTM)  $\delta^{30}$ Si<sub>DSi</sub> compositions, collected in March before the diatom bloom period, will be used here as baseline isotopic composition, in order to compare with open trap data and estimate the fractionation effect of diatoms ( $\epsilon_{dissolution}$ ). In this case,  $\delta^{30}$ Si<sub>DSi</sub> means are +2.28‰ (±0.09, 95% confidence; Table 1), although some variability is highlighted between data (e.g. mean

square weighted deviation (MSWD) = 4.1, n = 10; Table 1). ICP-MS data of diatom opal show that ratios of Al:Si are all < 0.01 (data not shown), indicating that contamination in all sediment trap and core samples is negligible. This was confirmed by visual inspection of the diatom samples by light microscopy, prior to analysis. Sediment trap diatoms are dominated (> 85 %) by the species *Synedra acus var radians*. Diatom concentrations show some variability, varying between c.  $3 \times 10^4$ and  $7 \times 10^4$  valves g<sup>-1</sup> wet weight (Fig. 3), although lowest concentrations are seen in the open sediment trap at 1350 m depth ( $3 \times 10^4$  valves g<sup>-1</sup> wet weight Fig. 3). This is coincident with lowest diatom (*S. acus var radians*) valve abundances also (86 %;



Table 2).  $\delta^{30}$ Si<sub>diatom</sub> data from the open sediment traps show little variability (within analytical uncertainty) down the water column profile in Lake Baikal (Table 2; Fig. 3) with values ranging from +1.11 and +1.38‰ (weighted mean +1.23‰ ± 0.06 at 95% confidence, MSWD = 2.9, *n* = 10). Sequencing (A) traps from May, July and August following the onset of major diatom productivity in early spring show a degree of variability with July and August  $\delta^{30}$ Si<sub>diatom</sub> data similar to the open sediment traps but data from May lower at 0.67‰ ±0.06 (Table 2). Surface sediment results from BAIK13-1C (0.6–0.8 cm core depth) and BAIK13-4F (0.2–0.4 cm core depth) are very similar to the both open (Z) and July, August sequencing (A) traps with  $\delta^{30}$ Si<sub>diatom</sub> signatures of +1.30‰ ± 0.08 (2 $\sigma$ ) and +1.43‰ ± 0.13 (2 $\sigma$ ) respectively (Table 2).

#### 5 Discussion

10

The extreme continentality of the region around Lake Baikal generates cold, dry winters that create an extensive ice cover over the lake from October/November-May/June (north basin) and January-April/May (south basin). This ice-cover plays a key role in regulating seasonal diatom productivity (as discussed in Sect. 2) with blooms develop-15 ing following the: (1) reductions in ice-cover in spring; and (2) mixed layer stratification in summer (Shimaraev et al., 1994; Popovskaya, 2000; Granin et al., 2000; Jewson et al., 2009; Troitskaya et al., 2014). These blooms are also coincident with periods of overturn in the upper waters of the lake (e.g. above the MTM; Sect. 2). The March  $\delta^{30}$ Si<sub>DSi</sub> data in this study were collected when there was no/negligible chlorophyll *a* in 20 the water column down to a depth of 200 m. Accordingly, we interpret March  $\delta^{30}$ Si<sub>DSi</sub> as reflecting the pre-spring bloom isotopic composition of silicic acid in the mixed layer prior to its uptake and fractionation in subsequent weeks as the spring bloom develops. Whilst the open traps deployed from March 2012-March 2013 may contain diatoms from both spring and autumnal blooms, we suggest that  $\delta^{30}$ Si<sub>diatom</sub> signatures from

<sup>25</sup> from both spring and autumnal blooms, we suggest that  $\delta^{50}$ Si<sub>diatom</sub> signatures from these traps are primarily derived from the spring bloom due to the dominance of: (1) spring diatom blooms in the annual record (Popovskaya, 2000); and (2) the dominance



of spring blooming *S. acus var radians* in the traps (> 85 % relative abundance; Fig. 3) (Ryves et al., 2003). Consequently, the open trap data should be reflective of spring silicic acid utilisation in the photic zone and so can be used to trace the fate of surface water signatures through the water column and into the sediment record.

# 5 5.1 Diatom $\delta^{30}$ Si fractionation ( $\epsilon$ )

25

During biomineralisation diatoms discriminate against the heavier <sup>30</sup>Si isotope, preferentially incorporating <sup>28</sup>Si into their frustules and leaving ambient waters enriched in <sup>30</sup>Si. Existing work from culture experiments and marine environments has suggested an *e* during biomineralisation ( $e_{uptake}$ ) of  $-1.1 \pm 0.4\%$  to  $-1.2 \pm 0.2\%$  (De La Rocha et al., 1997; Milligan et al., 2004; Varela et al., 2004; Fripiat et al., 2011). Our work, for the first time, extends this into lacustrine systems by suggesting a diatom fractionation effect ( $e_{uptake}$ ) of -1.05% (within uncertainty of previous estimates) based on a comparison of the mean pre-bloom spring top water (incorporating 0 to 180 m)  $\delta^{30}Si_{DSi}$  compositions of  $2.28\% \pm 0.09$  (95% confidence interval, n = 10) (Table 1) and the mean open sediment trap  $\delta^{30}Si_{diatom}$  of  $1.23\% \pm 0.06$  (95% confidence interval, n = 10) (Table 2). Evidence for a similar (within analytical uncertainty)  $e_{uptake}$  between marine and lacustrine systems both validates existing studies on freshwater systems (Alleman et al., 2005; Street-Perrott et al., 2008; Swann et al., 2010; Chapligin et al., 2012) and opens future applications of  $\delta^{30}Si_{diatom}$  analyses in these environments.

# <sup>20</sup> 5.2 The fate of diatom utilisation and $\delta^{30}Si_{diatom}$ in Lake Baikal

 $\delta^{30}$ Si<sub>diatom</sub> signatures through the open traps show minimal variation (mean of +1.23‰ ± 0.06 at 95% confidence and MSWD of 2.9, *n* = 10; Table 2). Similar values are also seen in the sequencing traps, except in May when values are considerably lower at +0.67‰ (±0.06; 2 $\sigma$ ). When applying the calculated  $\epsilon_{uptake}$  of -1.05‰ to the May (2012) data, a  $\delta^{30}$ Si<sub>DSi initial</sub> of between +1.66 to +1.78‰ (when taking into account the  $\delta^{30}$ Si<sub>diatom</sub> analytical variability of 2 $\sigma$ ) is estimated. These values fall outside



of the uncertainty of weighted mean March surface (namely depths above the MTM) water data ( $+2.28\% \pm 0.09$ , 95% confidence interval; Table 1). With diatom assemblages highlighting the prominence of spring diatom blooms in open traps, the discordance between these values is interesting. As discussed in Sect. 2, surface water

- <sup>5</sup> mixing occurs following ice off. It is possible that the lower composition of May signatures is due to this, although without  $\delta^{30}$ Si<sub>DSi</sub> of deeper March waters, we are unable to constrain these mixing compositions. As such, we cannot fully explain this lower value, yet maintain to compare open trap data and July, August sequencing trap data as mean values are within analytical uncertainty.
- <sup>10</sup> The isotopic composition of trap data (Table 2) from down the water column (except for the May sequencing trap) (Table 2) highlights that the isotopic signature incorporated into diatoms in the photic zone during biomineralisation is safely transferred through the water column without alteration, either from dissolution ( $\epsilon_{dissolution}$ ) or other processes. Although the majority of dissolution in Lake Baikal occurs at the surface-
- <sup>15</sup> sediment interface, with only 1 % of all diatoms from the photic zone becoming incorporated into the sediment record (Ryves et al., 2003),  $\delta^{30}$ Si<sub>diatom</sub> in sediment core surface samples (i.e., post burial) at BAIK13-1C (0.6–0.8 cm core depth) and at BAIK13-4F (0.2–0.4 cm core depth) of +1.30‰ ± 0.08 (2 $\sigma$ ) and +1.43‰ ± 0.13 (2 $\sigma$ ), respectively (Fig. 3) are also similar (within uncertainty) to the sediment trap data of 1.23‰ ± 0.06
- <sup>20</sup> (95% confidence). These data confirm that in contrast to previous work (Demarest et al., 2009) there is no  $\varepsilon_{dissolution}$  or at least no other alteration of the  $\delta^{30}$ Si<sub>diatom</sub> signature from diatoms sinking through the water column and during burial in the sediment record. This in agreement with previous studies on marine diatoms (Wetzel et al., 2014) and validates that  $\delta^{30}$ Si<sub>diatom</sub> can be used in lacustrine sediment cores to constrain bio-25 geochemical cycling (building on work by Egan et al., 2012).

# Discussion Paper **BGD** 12, 9369–9391, 2015 Insights into the transfer of silicon isotopes into the **Discussion** Paper sediment record V. N. Panizzo et al. **Title Page** Introduction Abstract Discussion Paper Conclusions References **Figures** Close Back **Discussion** Paper Full Screen / Esc **Printer-friendly Version** Interactive Discussion

#### 6 Conclusions

The first  $\delta^{30}$ Si<sub>diatom</sub> data from lacustrine sediment traps are presented from Lake Baikal, Siberia and their use in interpreting the fate of  $\delta^{30}$ Si<sub>diatom</sub> in the sediment record is shown. Mean values for open traps (+1.23‰ ± 0.06 at 95% confidence and MSWD

- of 2.9, n = 10), when compared with mean surface water March  $\delta^{30}$ Si<sub>DSi</sub> compositions (+2.28‰ ± 0.09 at 95% confidence) suggest a  $\epsilon_{uptake}$  of -1.05‰, which is in good agreement with published values from marine and other lacustrine systems of between -1.1 and -1.2‰. The near constant  $\delta^{30}$ Si<sub>diatom</sub> compositions in open traps demonstrates the full preservation of the signal through the water column and thereby
- <sup>10</sup> justifies the use and application of the technique in biogeochemical and palaeoenvironmental research. In particular, data highlight the absence of a fractionation factor associated with diatom dissolution ( $\epsilon_{dissolution}$ ) down the water column. This is further reinforced by lake surface sediment data from south basin cores, which also demonstrate the absence of  $e_{dissolution}$  due to the similar compositions (within uncertainty) of <sup>15</sup> surface sediment  $\delta^{30}$ Si<sub>diatom</sub> when compared to trap data.

Acknowledgements. This project was funded by National Environmental Research Council (NERC) Standard Grants NE/J00829X/1, NE/J010227/1 and NE/J007765/1 with research undertaken within the Centre of Environmental Geochemistry, a joint venture between the British Geological Survey and the University of Nottingham. The authors would like to thank Simon Chenery and Thomas Barlow (BGS) for ICP-MS analyses of dissolved silicon concentrations, in addition to Stephen Noble (NIGL) for his assistance and knowledge. Additional thanks go to Suzanne McGowan and Sarah Roberts (University of Nottingham) for their invaluable assistance in the field as well as the numerous other international colleagues that participated in the Lake Baikal March 2013 field season. The authors are indebted to the assistance of Nikolay

M. Budnev (Irkutsk State University), the captain and crew of the Geolog research boat and Dmitry Gladkochub (IEC) in facilitating and organising all Russian fieldwork. All <sup>210</sup>Pb dating was conducted at the Environmental Change Research Centre, University College London.



#### References

20

25

- Alleman, L. Y., Cardinal, D., Cocquyt, C., Plisnier, P. D., Descy, J. P., Kimirei, I., Sinyinza, D., and Andre, L.: Silicon isotopic fractionation in Lake Tanganyika and its main tributaries, J. Great Lakes Res., 31, 509–519, 2005. 9380
- Appleby, P. G. and Oldfield, F.: The calculation of <sup>210</sup>Pb dates assuming a constant rate of supply of unsupported <sup>210</sup>Pb to the sediment, Catena 5, 1–8, 1978. 9375
  - Atlas of Lake Baikal: "Siberia" Program Interdepartmental Scientific Committee of the SB RAS (in Russian Federal'naya Sluzhba Geodezii i Kartografii Rossii, Moscow), 1993.
- Cardinal, D., Alleman, L. Y., de Jong, J., Ziegler, K., and Andre, L.: Isotopic composition of silicon measured by multicollector plasma source mass spectrometry in dry plasma mode, J. Anal. Atom. Spectrom., 18, 213–218, 2003.
  - Chapligin, B., Meyer, H., Swann, G. E. A., Meyer-Jacob, C., and Hubberten, H.-W.: A 250 ka oxygen isotope record from diatoms at Lake El'gygytgyn, far east Russian Arctic, Clim. Past, 8, 1621–1636, doi:10.5194/cp-8-1621-2012, 2012. 9380
- <sup>15</sup> Cockerton, H. E., Street-Perrott, F. A., Leng, M. J., Barker, P. A., Horstwood, M. S. A., and Pashley, V.: Stable-isotope (H, O, and Si) evidence for seasonal variations in hydrology and Si cycling from modern waters in the Nile Basin: implications for interpreting the Quaternary record, Quaternary Sci. Rev., 66, 4–21, 2013. 9372, 9376

De La Rocha, C. L.: Opal-based isotopic proxies of paleoenvironmental conditions, Global Biogeochem. Cv., 20, GB4S09, doi:10.1029/2005GB002664, 2006. 9372

De La Rocha, C. L., Brzezinski, M. A., and DeNiro, M. J.: Fractionation of silicon isotopes by marine diatoms during biogenic silica formation, Geochim. Cosmochim. Ac., 61, 5051–5056, 1997. 9372, 9380

Demarest, M. S., Brzezinski, M. A., and Beucher, C. P.: Fractionation of silicon isotopes during biogenic silica dissolution, Geochim. Cosmochim. Ac., 73, 5572–5583, 2009. 9381

- Egan, K. E., Rickaby, R. E. M., Leng, M. J., Hendry, K. R., Hermoso, M., Sloane, H. J., Bostock, H., and Halliday, A. N.: Diatom silicon isotopes as a proxy for silicic acid utilisation: A Southern Ocean core top calibration, Geochim. Cosmochim. Ac., 96, 174–192, 2012. 9372, 9381
- <sup>30</sup> Falkner, K. K., Church, M., Measures, C., LeBaron, G., Touron, D., Jeandel, C., Stordal, M. C., Gill, G. A., Mortlock, R. A., and Froelich, P.: Minor and major element chamistry of Lake



Baikal, its tributaries, and surrounding hot springs, Limnol. Oceanogr., 42, 329–345, 1997. 9373

- Fripiat, F., Cavagna, A.-J., Dehairs, F., Speich, S., André, L., and Cardinal, D.: Silicon pool dynamics and biogenic silica export in the Southern Ocean inferred from Si-isotopes, Ocean
- Sci., 7, 533–547, doi:10.5194/os-7-533-2011, 2011. 9372, 9380
   Fripiat, F., Cavagna, A.-J., Dehairs, F., de Brauwere, A., André, L., and Cardinal, D.: Processes controlling the Si-isotopic composition in the Southern Ocean and application for paleo-ceanography, Biogeosciences, 9, 2443–2457, doi:10.5194/bg-9-2443-2012, 2012. 9372
- Georg, R. B., Reynolds, B. C., Frank, M., and Halliday, A. N.: New sample preparation techniques for the determination of Si isotopic compositions using MC-ICPMS, Chem. Geol., 235, 95–104, 2006, 9376
  - Granin, N. G., Jewson, D. H., Gnatovsky, R. Y., Levin, L. A., Zhdanov, A. A., Gorbunova, L. A., Tsekhanovsky, V. V., Doroschenko, L. M., and Mogilev, N. Y.: Turbulent mixing under ice an the growth of diatoms in Lake Baikal, Verhein Int. Ver. Lomnology, 27, 1–3, 2000. 9379
- <sup>15</sup> Gronskaya, T. P. and Litova, T. E.: Kratkaya Harakteristika Vodnogo Balansa Ozera Baikal za Period 1962–1988 (Short characteristics of the water balance of Lake Baikal during 1962– 1988), Gidrometeoizdsat, Leningrad, 1991. 9373
  - Hendry, K. R. and Brzezinski, M. A.: Using silicon isotopes to understand the role of the Southern Ocean in modern and ancient biogeochemistry and climate, Quaternary Sci. Rev., 89, 13–26, 2014. 9372
  - Hohmann, R., Kipfer, R., Peeters, F., Piepke, G., Imboden, D. M., and Shimaraev, M. N.: Deepwater renewal in Lake Baikal, Limnol. Oceanogr., 42, 841–855, 1997. 9374

20

- Hughes, H. J., Delvigne, C., Korntheuer, M., de Jong, J., Andre, L., and Cardinal, D.: Controlling the mass bias introduced by anionic and organic matrices in silicon isotopic measurements
- <sup>25</sup> by MC-ICP-MS, J. Anal. Atom. Spectrom., 26, 1892–1896, 2011. 9376, 9377 Jewson, D. H., Granin, N. G., Zhdanov, A. A., and Gnatovsky, R. Y.: Effect of snow depth on under-ice irradiance and growth of Aulacoseira baicalensis in Lake Baikal, Aquat. Ecol., 43, 673–679, 2009. 9379
  - Johnson, C. M., Beard, B. L., and Albarède, F.: Overview and general concepts, in: Geochem-
- <sup>30</sup> istry of Nontraditional Stable Isotopes, Reviews in Mineralogy and Geochemistry, edited by: Johnson, C. M., Beard, B. L., and Albarède, F., 1–24, 2004. 9378



Kipfer, R. and Peeters, F.: Some speculations on the possibility of changes in deep-water renewal in Lake Baikal and their consequences, in: Lake Baikal, edited by: Minoura, K., Elsevier, 2000. 9373

Kipfer, R., AeschbachHertig, W., Hofer, M., Hohmann, R., Imboden, D. M., Baur, H., Golubev, V.,

- and Klerkx, J.: Bottomwater formation due to hydrothermal activity in Frolikha Bay, Lake Baikal, eastern Siberia, Geochim. Cosmochim. Ac., 60, 961–971, 1996. 9374
  - Leng, M. J., Swann, G. E. A., Hodson, M. J., Tyler, J. J., Patwardhan, S. V., and Sloane, H. J.: The potential use of silicon isotope composition of biogenic silica as a proxy for environmental change, Silicon, 1, 65–77, 2009. 9372
- Mackay, A., Flower, R., Kuzmina, A., Granina, L., Rose, N., Appleby, P., Boyle, J., and Battarbee, R.: Diatom succession trends in recent sediments from Lake Baikal and their relation to atmospheric pollution and to climate change, Philos. T. R. Soc. B, 353, 1011–1055, 1998. 9375

Milligan, A. J., Varela, D. E., Brzezinski, M. A., and Morel, F. O. M. M.: Dynamics of silicon

- metabolism and silicon isotopic discrimination in a marine diatom as a function of  $pCO_2$ , Limnol. Oceanogr., 49, 322–329, 2004. 9372, 9380
  - Müller, B., Maerki, M., Schmid, M., Vologina, E. G., Wehrli, B., Wuest, A., and Sturm, M.: Internal carbon and nutrient cycling in Lake Baikal: sedimentation, upwelling, and early diagenesis, Global Planet. Change, 46, 101–124, 2005. 9373
- Opfergelt, S., Eiriksdottir, E. S., Burton, K. W., Einarsson, A., Siebert, C., Gislason, S. R., and Halliday, A. N.: Quantifying the impact of freshwater diatom productivity on silicon isotopes and silicon fluxes: Lake Myvatn, Iceland, Earth. Planet. Sc. Lett., 305, 73–82, 2011. 9372
  - Pichevin, L. E., Reynolds, B. C., Ganeshram, R. S., Cacho, I., Pena, L., Keefe, K., and Ellam, R. M.: Enhanced carbon pump inferred from relaxation of nutrient limitation in the glacial ocean, Nature, 459, 1114–1198, 2009. 9372
  - Popovskaya, G. I.: Ecological monitroing of phytoplankton in Lake Baikal, Aquat. Ecosyst. Health, 3, 215–225, 2000. 9379

25

- Ravens, T. M., Kocsis, O., Wuest, A., and Granin, N.: Small-scale turbulence and vertical mixing in Lake Baikal, Limnol. Oceanogr., 45, 159–173, 2000. 9373
- Ryves, D. B., Jewson, D. H., Sturm, M., Battarbee, R. W., Flower, R. J., Mackay, A. W., and Granin, N. G.: Quantitative and qualitative relationships between planktonic diatom communities and diatom assemblages in sedimenting material and surface sediments in Lake Baikal, Siberia, Limnol. Oceanogr., 48, 1643–1661, 2003. 9373, 9380, 9381



9386

Zhdanov, A. A.: Deep ventilation of Lake Baikal waters due to spring thermal bars, Limnol. Oceanogr., 38, 1068–1072, 1993. 9374
Shimaraev, M., Verbolov, V., Granin, N., and Sherstyankin, P.: Physical limnology of Lake Baikal: A Review, Baikal International Centre for Ecological Research, 1–89, 1994. 9373, 9379

Akad. Nauk, 408, 102–107, 2006. 9373

5

<sup>10</sup> Street-Perrott, F. A., Barker, P. A., Leng, M. J., Sloane, H. J., Wooller, M. J., Ficken, K. J., and Swain, D. L.: Towards an understanding of late Quaternary variations in the continental biogeochemical cycle of silicon: multi-isotope and sediment-flux data for Lake Rutundu, Mt Kenya, East Africa, since 38 ka BP, J. Quaternary Sci., 23, 375–387, 2008. 9380

Sherstyankin, P. P., Alekseev, S. P., Abramov, A. M., Stavrov, K. G., De Batist, M., Hus, R.,

Shimaraev, M. N., and Granin, N. G.: Temperature stratification and the mechanisms of con-

Canals, M., and Casamor, J. L.: Computer-based bathymetric map of Lake Baikal, Dokl.

vection in Lake Baikal, Dokl. Akad. Nauk, 321, 1991. Shimaraev, M. N., Granin, N. G., and

Swann, G. E. A., Leng, M. J., Juschus, O., Melles, M., Brigham-Grette, J., and Sloane, H. J.:

- A combined oxygen and silicon diatom isotope record of Late Quaternary change in Lake El'gygytgyn, North East Siberia, Quaternary Sci. Rev., 29, 774–786, 2010. 9380
  - Tréguer, P. J., and De La Rocha, C. L.: The world ocean silica cycle, Ann. Rev. Mar. Sci., 5, 477–501, 2013. 9372

Troitskaya, E., Blinov, V., Ivanov, V., Zhdanov, A., Gnatovsky, R., Sutyrina, E., and Shi-

- <sup>20</sup> maraev, M.: Cyclonic circulation and upwelling in Lake Baikal, Aquat. Sci., 77, 171–182, doi:10.1007/s00027-014-0361-8, 2014. 9373, 9379
  - Varela, D. E., Pride, C. J., and Brzezinski, M. A.: Biological fractionation of silicon isotopes in Southern Ocean surface waters, Global Biogeochem. Cy., 18, doi:10.1029/2003GB002140, 2004. 9372, 9380
- Weiss, R. F., Carmack, E. C., and Koropalov, V. M.: Deep-water renewal and biological production in Lake Baikal, Nature, 349, 665–669, 1991. 9374
  - Wetzel, F., de Souza, G. F., and Reynolds, B. C.: What controls silicon isotope fractionation during dissolution of diatom opal?, Geochim. Cosmochim. Ac., 131, 128–137, 2014. 9372, 9381



**Table 1.** DSi concentrations (ppm),  $\delta^{30}$ Si<sub>DSi</sub> (‰) and  $\delta^{29}$ Si<sub>DSi</sub> (‰) with respective analytical uncertainties for South Basin sites BAIK13-1a and b. Dates of sampling are provided. Uncertainties are  $2\sigma$  unless stated and the weighted average of samples, their 95% confidence interval and population MSWD are also presented. Data are plotted in Fig. 2.

	Depth (m)	DSi (ppm)	$\delta^{30} {\rm Si}_{\rm DSi}$	Prop' 2s abs	$\delta^{29} {\rm Si}_{\rm DSi}$	Prop' 2s abs
BAIK13-1a	0.4	1.22	2.34	0.15 <sup>2</sup>	1.22	0.10 <sup>2</sup>
3 Mar 2013	10	1.19	2.17	0.15 <sup>2</sup>	1.18	0.09 <sup>2</sup>
	24	1.17	2.55	0.15 <sup>2</sup>	1.29	0.10 <sup>2</sup>
	40	1.12	2.18	0.11	1.18	0.06
	100	1.06	2.22 <sup>1</sup>	0.31	1.27 <sup>1</sup>	0.19
	180	0.66	2.40	0.08	1.23	0.04
BAIK13-1b	1	0.74	2.16	0.09	1.14	0.04
12 Mar 2013	10	1.21	2.44	0.15 <sup>2</sup>	1.20	0.05 <sup>2</sup>
	20	1.15	2.28	0.10 <sup>2</sup>	1.17	0.04 <sup>2</sup>
	50	1.16	2.29	0.16 <sup>2</sup>	1.26	0.11 <sup>2</sup>
W.A MEAN MSDW			2.28 4.1	<b>0.09</b> <sup>2</sup>	1.19 1.9	<b>0.03</b> <sup>2</sup>

<sup>1</sup> This water sample was not pre-concentrated, refer to methods.

 $^2$  These water sample values are weighted averages for sample replicates that are analytically robust. These errors are at the 95 % confidence interval.



**Table 2.** Open and sequencing trap (sampling interval 2012–2013)  $\delta^{30}$ Si<sub>diatom</sub> data and respective uncertainties (2 $\sigma$ ). Mean values for open trap  $\delta^{30}$ Si<sub>diatom</sub> compositions are provided along with 95% confidence and the population MSWD value (in bold). Respective water column depths are presented along with the relative abundance of *S. acus var radians* (data not available for sequencing traps). All open trap data (Z2–Z11) are plotted in Fig. 3.

Code	Depth (m)	$\delta^{30} { m Si}_{ m DSi}$	Prop' 2s abs	$\delta^{29} Si_{DSi}$	Prop' 2s abs	S. acus var radians		
Open Sediment Traps								
Z2	100	1.19 ່	0.12	0.62	0.07	90%		
Z3	200	1.28	0.11	0.70	0.06	90 %		
Z4	300	1.11 <sup>1</sup>	0.15	<b>0.61</b> <sup>1</sup>	0.08	93%		
Z5	400	1.32 <sup>1</sup>	0.16	<b>0.69</b> <sup>1</sup>	0.10	93%		
Z6	600	1.38 <sup>1</sup>	0.15	<b>0.71</b> <sup>1</sup>	0.10	88%		
Z7	700	1.38	0.17	0.69	0.11	94 %		
Z8	900	1.26	0.14	0.66	0.10	92%		
Z9	1100	1.21	0.13	0.60	0.10	94 %		
Z10	1300	1.17 <sup>1</sup>	0.12	<b>0.61</b> <sup>1</sup>	0.07	92%		
Z11	1350	1.25	0.11	0.62	0.10	86 %		
W.A Mean		1.23	0.06 <sup>1</sup>	0.63	0.03 <sup>1</sup>			
MSWD		2.9		1.6				
Sequencing Traps								
A4	May	0.67	0.06	0.36	0.04			
A6	Jul	1.22	0.08	0.53	0.09			
A7	Aug	1.37	0.07	0.69	0.03			
Mean		1.09	0.74 (2 SD)	0.53	0.33 (2 SD)			
Sediment Cores								
BAIK13-1C	0.6–0.8 cm	1.30	0.08	0.68	0.05			
BAIK13-4F	0.2–0.4 cm	1.43	0.13	0.75	0.04			

<sup>1</sup>Uncertainty is 95 % confidence.

<b>BGD</b> 12, 9369–9391, 2015					
Insights into the transfer of silicon isotopes into the sediment record					
V. N. Pan	V. N. Panizzo et al.				
Title	Title Page				
Abstract	Introduction				
Conclusions	References				
Tables	Figures				
14	×				
	•				
Back	Close				
Full Screen / Esc					
Printer-friendly Version					
Interactive Discussion					

**Discussion** Paper

**Discussion Paper** 

**Discussion** Paper

**Discussion** Paper



**Figure 1.** Map of the Lake Baikal catchment, showing dominant inflowing rivers and the Angara river outflow. The three catchments are identified as well as the location of sites BAIK13-1 and BAIK13-4, where cores, sediment traps and water column profiles were collected.











**Figure 3.** Open sediment trap (2012–2013) data from site BAIK13-1, south basin Lake Baikal. Samples are displayed along a *y* axis of water column depth.  $\delta^{30}$ Si<sub>diatom</sub> data (‰) are expressed with respective analytical errors (2 $\sigma$ ) and surface sediment samples from cores BAIK13-1C and BAIK13-4F are also displayed as brown symbols. In addition a reference line of mean  $\delta^{30}$ Si<sub>diatom</sub> open trap compositions is highlighted and the calculated a  $\varepsilon_{uptake}$  of -1.05‰ based on the surface water mean endmember of +2.28‰ (shown in blue). Percentage abundance of the dominant diatom *Synedra acus var radians* and diatom concentrations (valves g<sup>-1</sup> wet weight) are also provided.

